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STUDY OF GROWTH PARAMETERS FOR REFRACTORY CARBIDE SINGLE CRYSTALS

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CONTENTS

ILLUSTRATIONS

I INTRODUCTION

Interest in the refractory carbides has increased recently in anticipation of many new applications requiring the use of super-refractories. However, during the research and development work on these materials, difficulties have been encountered in attaining and reproducing desired physical properties. Little is known about ultimate intrinsic physical properties or about the influences of stoichiometric changes, impurities, and grain boundaries on these properties. In obtaining this type of information, single crystals of various carbide compositions would be of great value. At present, the only crystals readily available are of titanium carbide, grown by the Verneuil process, and little is known of their structure and perfection.

Stanford Research Institute has been engaged by the National Aeronautics and Space Administration to investigate the application of new techniques and procedures to the growth of single crystals of tantalum carbide, hafnium carbide, and solid solutions of these carbides. The new techniques being investigated fall into two classes: (1) utilization of a-c arc melting for Verneuil crystal growth; and (2) application of recently developed methods of liquid metal solution growth of crystals.

II SUMMARY AND CONCLUSIONS

During this reporting period the new arc-Verneuil crystal growing furnace was installed and tantalum carbide crystal growth experiments were resumed. Mechanical operation of the crystal grower is satisfactory; it produces uniform operating conditions and symmetrically shaped boules. However, a major impediment to tantalum carbide (TaC) crystal growth is decarburization of the boule, which occurs in all atmospheres in which a low voltage a-c arc is stable. Under operating conditions which provide improved stoichiometry ratios (>10% hydrogen), arc stability is still quite poor. Hafnium carbide and tantalum-hafnium carbide powders in a size range suitable for crystal growth have been ordered; crystal growth of these materials will be initiated as soon as the powders are received.

Metal solution (menstruum) growth experiments have not yielded tantalum carbide crystals larger than 0.2 mm. Further work in this area has therefore been discontinued.

III CRYSTAL GROWTH STUDIES

A. Arc-Verneuil Growth

1. Apparatus

The new arc-Verneuil furnace chamber was received and installed during March. Axes of the three horizontal electrodes and the seed holder of the crystal grower form a common intersection which deviates less than 0.010 inch during rotation of all four members. Some difficulties were encountered with the primary vacuum seal for the horizontal electrodes. Since delivery lead time for the Viton quad-rings used in this seal was 9 weeks, the seal was redesigned to employ O-rings. Operation with a Viton O-ring seal is satisfactory if periodic replacements of overheated seals are made. Larger motors for rotating the electrodes have been substituted for the original motors, and some of the original electrode bushings have been replaced with bushings that are more concentric. With these minor changes, operation of the furnace apparatus is good. The shape symmetry of boules is much better than was possible with the previous apparatus; an example is shown in Fig. 1. The modified a-c arc power supply works satisfactorily; no difficulties have been encountered in providing sufficient power.

The initial tantalum carbide crystal growth experiments were made with the audio-driven pulsed-bed particle feeder described in the eighth Quarterly Status Report. The principal disadvantage of this powder feeder is its small powder storage capacity, which is limited by the tendency of excess powder to overdamp the vibrating sieve and prevent particle flow. Since the storage capacity of tantalum carbide is marginal for growth of a complete boule, a METCO feeder was eventually substituted for the audio-driven feeder.

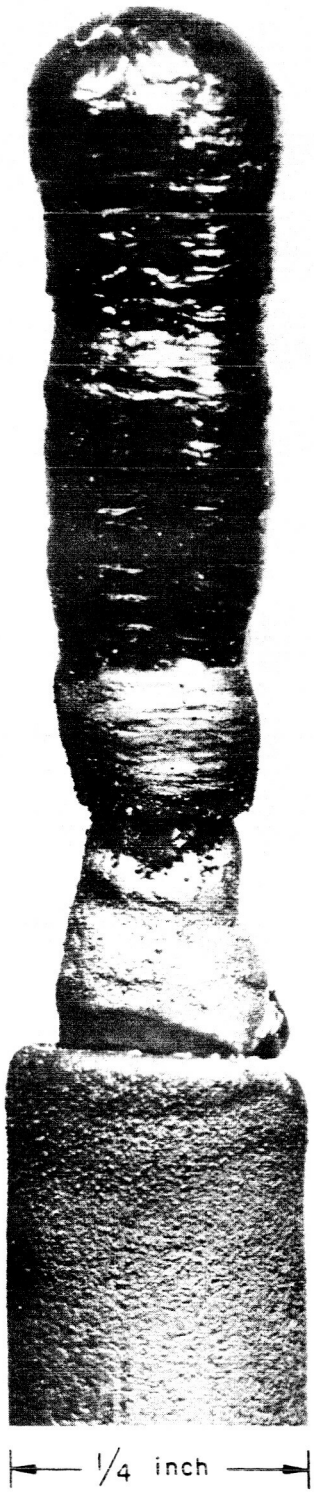

FIG. 1 TANTALUM CARBIDE BOULE (TaC_{1-x}) GROWN IN THE ARC-VERNEUIL FURNACE (5-27-66)

2. Experimental Results

A series of runs was made to explore operating parameters of the new furnace and modified power supply, which are suitable for the growth of tantalum carbide (TaC) boules. Initially, in these runs, the hot-pressed tantalum carbide "seeds" usually fractured when the arc was struck. This apparently was caused by the fact that the minimum power output of the modified power supply is considerably higher that that in the previous unit. Thus, when the arc is initiated, the seed is now severely shocked thermally. On the other hand, growth of a boule directly on a graphite foot usually results in spalling of the boule at the interface because of poor adhesion. This problem has been circumvented by using short tantalum plugs, 1/8-inch in diameter, inserted in the top of the seed holder. The tantalum melts to form a base upon which tantalum carbide is securely welded prior to growth of the boule. However, if it is necessary to restrike the arc after a temporary power failure of all three electrodes, the boule usually fractures.

Loss of carbon from the carbide boule is one of the major obstacles to be overcome in growing single-phase crystals. Our previous work has indicated that hydrogen additions to the environment greatly restrict the extent of carbon loss. However, hydrogen and acetylene additions to argon in excess of 5% at 0.5 to 1 atm total pressure cause considerable arc instability. Although improved arc stability is attained at lower pressures, the rate of decarburization of the carbide simultaneously increases. In 5% to 7% hydrogen at a total pressure of 0.5 atm arc performance is stable and yields a boule with very little subcarbide (Ta_2C). The subcarbide that is present usually decorates subgrain boundaries located near the boule surface. Although the external surfaces of these boules are yellow, probably because of recarburization during cooling, cross-sectioned surfaces are metallic gray. The carbon content by X-ray lattice parameter measurement is in the lower region of the tantalum carbide phase field. Although boules grown in acetylene have not been sectioned for carbon analysis, there is no apparent advantage to the use of acetylene in stablizing the arc. The primary

tantalum carbide grain size continues to be similar to the grain size observed in our previous experiments. Usually three to six grains are intersected by a longitudinal cross section of the boule.

Most of the present effort is directed toward increasing the carbon content of tantalum carbide boules. For this purpose, several runs were made to determine the feasibility of maintaining molten tantalum carbide within a small crucible cup drilled in the top of a graphite seedholder. The graphite walls maintain a high carbon stoichiometry in tantalum carbide, and conceivably one could utilize a hot graphite shell in close proximity, surrounding the molten cap of the boule, to assist in control of the final crystal composition. Tantalum carbide bars 1/8-inch in diameter were melted in a 1/4-inch OD graphite rod with the present saturable-core reactor power supply. The color of the tantalum carbide in cross section remained yellow, which indicates a high carbon content. The subcarbide (Ta_2C) was not present. Unfortunately, erosion of the graphite crucible, even with an argon blanket, is very rapid and the graphite container disappears almost as fast as tantalum carbide melting occurs. Consequently it is very difficult to solidify tantalum carbide at a slow rate under controlled conditions.

In principle, a high voltage arc-stabilizing circuit can be superimposed on the low voltage power supply circuit to ensure that the arc will not extinguish under marginal operating conditions. This may be done by using a high frequency generator and a suitable inductance to isolate the high frequency signal from the 60-cycle a-c power supply, as shown in Fig. 2. A 500-kc, 3000-volt, 10-watt oscillator power supply was constructed to test its capacity to maintain an arc on one of the electrodes. The test results indicated that too much of the high frequency power was lost in the inductance used to isolate the low voltage power supply. A larger generator (300-watt radio transmitter) is being adapted for a similar test at a frequency of 2 mc.

Vacuum-fired, reactor grade, hafnium carbide and mixed solid solution carbide powders (-200 +325) have been ordered from Wah Chang Corporation, Albany, Oregon, and are expected to arrive by July 1, 1966.

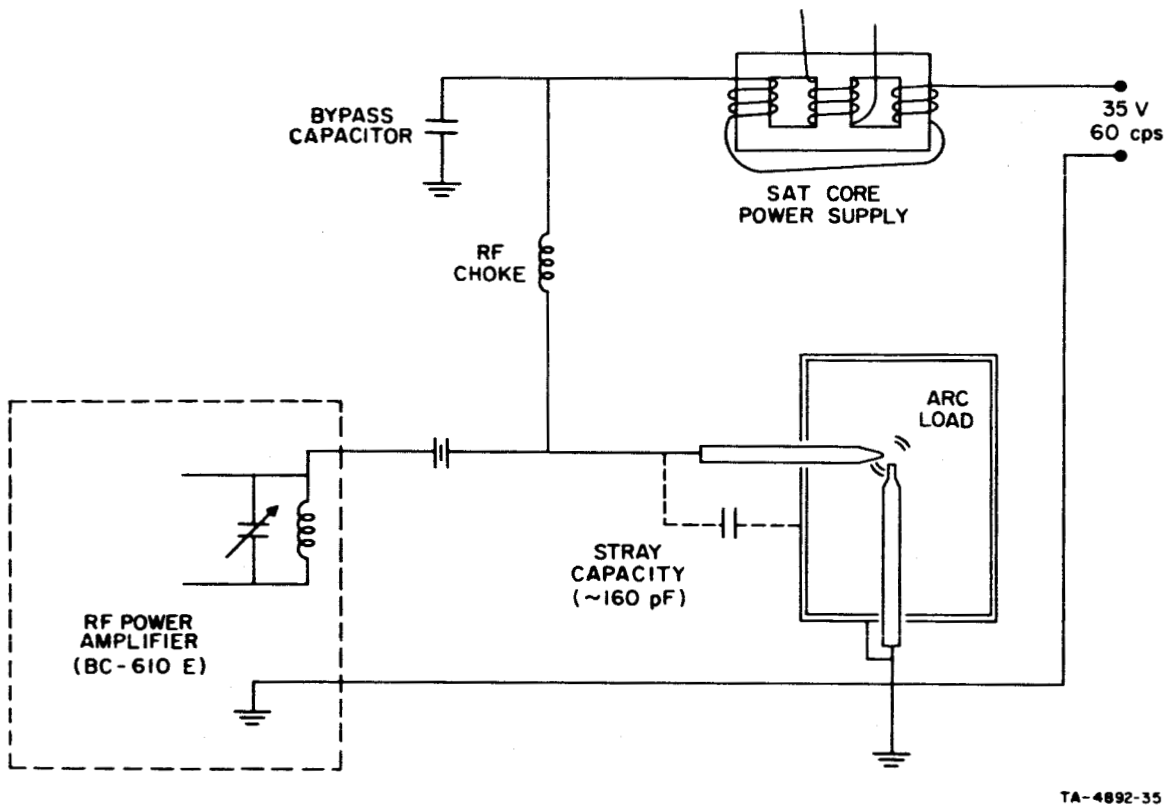

FIG. 2 CIRCUIT FOR SUPERIMPOSING A HIGH FREQUENCY STABILIZING SIGNAL ON THE ARC-ELECTRODE

B. Metal Solution Growth

Additional experiments were made in an attempt to transfer tantalum carbide from a nutrient zone across a liquid metal solution zone approximately 1/4-inch thick to a seed area for growth of tantalum carbide. These were extensions of experiments described in more detail in the eighth Quarterly Status Report. Liquid platinum dissolves tantalum and some carbon. Platinum was used as the solvent in order to permit gravity separation of the seed, which was attached at the bottom of the container, and the tantalum carbide nutrient particles floating on the platinum solvent. Although the experiment was terminated after three hours because of a heating element failure, there was no evidence of significant dissolution and transfer of tantalum carbide to the seed. Insufficient thermochemical data are available to calculate the platinum solution concentration of tantalum in equilibrium with tantalum carbide but it is expected to be less than 1 at. %.

Temperature gradient solution growth of tantalum carbide single crystals larger than 0.2 mm and, in particular, growth on seed crystals has been prevented by homogeneous nucleation within the saturated solution near the seed. To prevent nucleation, lower temperature gradients are evidently required. Because of the low tantalum carbide equilibrium solubility in liquid metals, long experiment times are also required to compensate for the slow growth rate. A 66-hour experiment was conducted in an Al_2O_3 crucible using an iron solution with tantalum carbide powder as a nutrient. Seed crystals were placed on an Al_2O_3 dish and submerged in the solution. A temperature difference of about 100°C was maintained between the cooler base of the crucible and the solution surface. This was deemed to be the minimum temperature difference that would ensure a small but properly directed temperature gradient to the seed crystals. No evidence for growth of tantalum carbide on seeds was obtained.

The transfer experiment involving a boron nitride crucible and a zone of liquid iron reported in Quarterly Status Report No. VIII was repeated. The tantalum carbide transfer from the polycrystalline nutrient to the seed occurs because of intergranular solution and separation of nutrient tantalum carbide grains within the hot-pressed tantalum carbide billet. Thus, a major fraction of the tantalum carbide is transferred as solid particles rather than chemically by the solution.

Because of the low equilibrium solubility of tantalum carbide and hafnium carbide in liquid metals at temperatures where then can be contained without chemical side reactions in available crucible materials, and because of the ease of homogeneous nucleation of tantalum carbide within the liquid metal alloys investigated, growth of tantalum carbide and hafnium carbide crystals as large as one cm in liquid metal solutions does not appear as promising as does growth by the arc-Verneuil method. Work on the solution method is therefore being discontinued for this investigation.

IV FUTURE WORK

Future work will include growth of hafnium carbide and mixed solid solution carbide boules, for which the relative decarburization rate is not expected to be as severe as that for tantalum carbide. The work with tantalum carbide will emphasize methods for increasing the carbon content of boules and for eliminating grain boundaries of the primary tantalum carbide phase. These efforts will include: (1) use of the high frequency arc stabilizing circuit; (2) use of fluidized fine carbon particles in the arc region; (3) mixing carbon particles with the carbide feed powder; and (4) the use of vapor sources of carbon other than hydrocarbons. Of particular interest are freon (F_2CCl_2) and carbon tetrachloride (CCl_4).